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(71) Applicant: **Takachiho Chemical Industrial Co., Ltd.**
Tokyo 150-0012 (JP)

(72) Inventors:
• **NAKANOYA, Tsutomu**,
Takachiho Chem. Ind. Co., Ltd.
Machida-shi, Tokyo 194-0004 (JP)
• **SHIBUSAWA, Yuji**,
Takachiho Chem. Ind. Co., Ltd.
Machida-shi, Tokyo 194-0004 (JP)

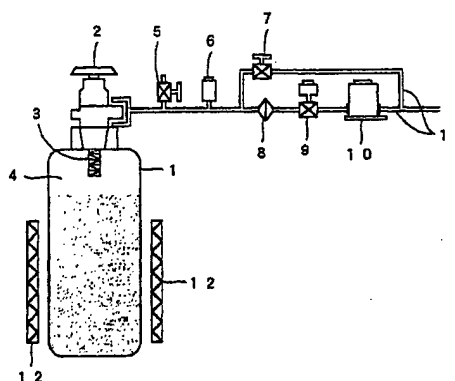
• **HASUMI, Kazuhiro**,
Takachiho Chem. Ind. Co., Ltd.
Machida-shi, Tokyo 194-0004 (JP)
• **ISHIMORI, Koji**, **Takachiho Chem. Ind. Co., Ltd.**
Machida-shi, Tokyo 194-0004 (JP)
• **IBARAKI, Satoshi**
Osaka-shi, Osaka 552-0004 (JP)
• **TAKAUCHI, Akira**
Osaka-shi, Osaka 534-0016 (JP)

(74) Representative: **Glawe, Delfs, Moll & Partner**
Patentanwälte
Postfach 26 01 62
80058 München (DE)

(54) **METHOD AND APPARATUS FOR STORING AND FEEDING GASEOUS COMPOUND**

(57) The present invention is directed to a method of and an apparatus for adsorbing a gaseous hydrogenated compound or a gaseous halogenated compound to high-purity activated carbon under a storage environment at a pressure which is not more than atmospheric pressure and storing the adsorbed gaseous compound upon bringing the gaseous compound into contact with the activated carbon, and desorbing at least a part of the adsorbed gaseous compound and delivering the part to a work environment, wherein the activated carbon is treated by a series of steps comprising a step of adsorbing the gaseous hydrogenated compound or the gaseous halogenated compound upon bringing the gaseous compound into contact with the activated carbon in advance in a sealed space, a step of accelerating a reaction of a system passing through the adsorbing step, and a step of expelling the gaseous compound passing through the reaction accelerating step from the sealed space.

Fig 1



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however, an anion in the acid used for washing may, in some cases, remain in the activated carbon. When such activated carbon is used for adsorption and storage of arsine, phosphine, or the like, nitrogen gas, oxygen gas, or the like is generated due to reduction of the anion, resulting in danger that the purity of the stored gas is decreased, and arsine, for example, leaks outward by the rise in the pressure inside the bomb, as in the above-mentioned case.

[0011] In a case where high-purity activated carbon produced using a high-purity raw material is used, the problem that arsine decomposes into arsenic and hydrogen, for example, is avoided. However, the high-purity activated carbon and a gaseous compound such as arsine react with each other, to generate impurities such as hydrogen, nitrogen, carbon monoxide and carbon dioxide. The impurity gas generated in this case differs from hydrogen gas generated by the above-mentioned self-decomposition of arsine or the like in that the gas pressure in a storage container does not generally reach not less than atmospheric pressure. Consequently, there is little danger that arsine or the like leaks outward. When a gaseous compound such as arsine, phosphine, or boron trifluoride is used in an ion implantation process in the semiconductor industry, for example, however, the purity of the gaseous compound must be not less than 99.9 % according to the SEMI International Standards (1990). When the impurity gases are generated, as described above, therefore, the purity of the gaseous compound is decreased, thereby significantly degrading the value of the gaseous compound.

[0012] In a case where a particular gaseous hydrogenated compound or gaseous halogenated compound, such as arsine, phosphine, or boron trifluoride, is stored upon being adsorbed to activated carbon under the temperature of a normal work environment, when it is sucked in, desorbed and delivered using a vacuum pump while controlling the flow rate of the gaseous compound, the gaseous compound finally remains to some extent in the container, which depends on the flow rate of the gaseous compound and the performance of the vacuum pump, so that the amount of the gaseous compound which can be effectively utilized is decreased.

[0013] An object of the present invention is to solve the above-mentioned various problems, and to provide a method of and an apparatus for efficiently adsorbing a gaseous hydrogenated compound or a gaseous halogenated compound such as arsine, phosphine, or boron trifluoride, safely and stably storing the gaseous compound in a considerable amount, preventing the gaseous compound from being released to atmosphere, and safely and efficiently delivering the gaseous compound.

Disclosure of the Invention

[0014] In the present invention, developed is a method of bringing a gaseous hydrogenated compound or a gaseous halogenated compound in a predetermined amount into contact with activated carbon composed of a phenol resin as a main raw material, adsorbing the gaseous compound to the activated carbon under a storage environment at a pressure which is not more than atmospheric pressure and storing the adsorbed gaseous compound, and desorbing at least a part of the adsorbed gaseous compound and delivering the part to a work environment.

[0015] In the present invention, developed is an apparatus for bringing a gaseous hydrogenated compound or a gaseous halogenated compound in a predetermined amount to be used into contact with activated carbon composed of a phenol resin as a main raw material, adsorbing the gaseous compound to the activated carbon under a storage environment at a pressure which is not more than atmospheric pressure and storing the adsorbed gaseous compound, and desorbing at least a part of the adsorbed gaseous compound and delivering the part to a work environment.

[0016] In the present invention, developed are a method of and an apparatus for using, as activated carbon composed of a phenol resin as a main raw material which is used for the above-mentioned method and apparatus, a granular carbon formed product obtained by bonding activated particles formed by carbonizing phenol resin powder, which has a specific surface area of 700 to 1500 m²/g, has pores having a pore diameter of 0.01 to 10 μm, the pore volume of which is 0.1 to 1.0 cc/g, has pores having a pore diameter of not more than 10 nm, the pore volume of which is 0.20 to 0.80 cc/g, and containing not less than 75 % by volume pores having a pore diameter of 0.6 to 0.8 nm, has a bulk density of 0.4 to 1.1 g/cc, has a packing density of 0.30 to 0.70 g/cc, has an ash content of not more than 1.0 %, and has a tensile strength of not less than 30 kg/cm².

[0017] In the present invention, developed is a method of treating activated carbon by a series of steps comprising a step of adsorbing a gaseous hydrogenated compound or a gaseous halogenated compound upon bringing the gaseous compound into contact with activated carbon in advance in a sealed space, a step of accelerating a reaction of a system passing through the adsorbing step, and a step of expelling the gaseous compound passing through the reaction accelerating step from the sealed space, to prevent, when a gaseous hydrogenated compound or a gaseous halogenated compound of a type which is the same as or different from that of the gaseous compound is adsorbed to be stored, one or more impurity gases from being generated by contact between the activated carbon and the stored gaseous compound and prevent the purity of the stored gaseous compound from being decreased.

[0018] In the present invention, developed is an apparatus for treating activated carbon by a series of steps comprising a step of adsorbing a gaseous hydrogenated compound or a gaseous halogenated compound upon bringing the gaseous compound into contact with activated carbon in advance in a sealed space, a step of accelerating a

oride upon bringing the gaseous compound into contact with the activated carbon in advance in a sealed space, a step of accelerating a reaction of a system passing through the adsorbing step, and a step of expelling the gaseous compound passing through the reaction accelerating step from the sealed space.

[0025] The specific surface area of the activated carbon is preferably 700 to 1500 m²/g as described above, and is more preferably 850 to 1400 m²/g, and still more preferably 900 to 1300 m²/g. The reason for this is that it is not preferable that the specific surface area of the activated carbon is less than 700 m²/g because the total amount of adsorbed portions of the gaseous compound such as arsine or phosphine is so small that the adsorption capacity becomes small, while it is not preferable that the specific surface area is not less than 1500 m²/g because the pore volume of the pores having a pore diameter of 0.6 to 0.8 nm, which are considered to effectively function in adsorbing the gaseous compound such as arsine or phosphine becomes small.

[0026] In the activated carbon, the pore volume of the pores having a pore diameter of 0.01 to 10 μm is preferably 0.1 to 1.0 cc/g, as described above, more preferably 0.2 to 0.8 cc/g, and still more preferably 0.3 to 0.7 cc/g. The reason for this is that it is not preferable that the pore volume of the pores having a pore diameter of 0.01 to 10 μm is less than 0.1 cc/g because the diffusion rate in the pores of the gaseous compound such as arsine or phosphine becomes low so that the adsorption rate and the desorption rate decrease, while it is not preferable that the pore volume of the pores having a pore diameter of 0.01 to 10 μm is more than 1.0 cc/g because the bulk density and the mechanical strength of the activated carbon become low.

[0027] It is preferable that the pore volume of the pores having a pore diameter of not more than 10 nm is 0.20 to 0.80 cc/g, and the ratio of the pore volume of the pores having a pore diameter of 0.6 to 0.8 nm to the pore volume of the pores having a pore diameter of not more than 10 nm is not less than 75 %. The pore volume of the pores having a pore diameter of not more than 10 nm is preferably 0.30 to 0.70 cc/g, and more preferably 0.30 to 0.60 cc/g. The reason for this is that it is not preferable that the pore volume of the pores having a pore diameter of not more than 10 nm becomes small because the pore volume of the pores having a pore diameter of 0.6 to 0.8 nm also decreases so that the adsorption capacity of the gaseous compound such as arsine or phosphine decreases, while it is not preferable that the pore volume of the pores having a pore diameter of not more than 10 nm is too large because the ratio of the pore volume of the pores having a pore diameter of 0.6 to 0.8 nm decreases.

[0028] The ratio of the pore volume of the pores having a pore diameter of 0.6 to 0.8 nm to the pore volume of the pores having a pore diameter of not more than 10 nm is not less than 75 %, preferably not less than 78 %, and most preferably not less than 80 %. As a result of respectively calculating the major axes of molecules of arsine (AsH₃) and phosphine (PH₃) using the van der Waals radii of the molecules with respect to a structure in which the sizes of the molecules are calculated using the molecule mechanics, they are approximately 0.45 nm and 0.49 nm. However, pores which effectively function in adsorbing the molecules are pores having a diameter slightly larger than the diameters of the molecules, which are considered to be pores having a pore diameter of 0.6 to 0.8 nm. Pores having a pore diameter, which is much smaller than the sizes of the molecules, are not preferable because the adsorption rate of the molecules becomes low. It is not preferable that the pore diameter is significantly larger than the sizes of the molecules because the desorption rate becomes high simultaneously with the adsorption rate so that the amount of equilibrium adsorption decreases.

[0029] Therefore, it is not preferable that the ratio of the pore volume of the pores having a pore diameter of 0.6 to 0.8 nm, which effectively function in adsorbing the molecules, to the pore volume of the pores having a pore diameter of not more than 10 nm is less than 75 % because the adsorption capacity of the gaseous compound such as arsine (AsH₃) or phosphine (PH₃) decreases.

[0030] The bulk density of particles of the activated carbon is preferably 0.4 to 1.2 g/cc, as described above, more preferably 0.5 to 1.0 g/cc, and still more preferably 0.6 to 0.8 g/cc. The reason for this is that it is not preferable that the bulk density is too low because the adsorptivity per unit volume in a container such as a bomb decreases when the activated carbon is packed into the container, while it is not preferable that the bulk density is too high because the absorptivity decreases due to the decrease in the continuity of the pores of the activated carbon.

[0031] The packing density in a case where the activated carbon is packed into the container such as the bomb is preferably 0.3 to 0.7 g/cc, as described above, and more preferably 0.5 to 0.65 g/cc. The reason for this is that it is not preferable that the packing density is too low because the adsorptivity per unit volume in the container decreases. The shape of the activated carbon used in the present invention may be in a cylindrical shape or shapes having other irregular cross sections in addition to a columnar shape or a spherical shape.

[0032] The size of the particles of the activated carbon is 0.3 to 5 mm, preferably 0.6 to 4 mm, and more preferably 0.8 to 3 mm. The reason for this is that it is not preferable that the particles are too large because the packing density cannot be increased when the activated carbon is packed into the container such as the bomb, while it is not preferable that the particles are too small because the workability is degraded at the time of producing the particles and at the time of packing the activated carbon into the container.

[0033] The reason why the activated carbon is treated by being subjected to a series of steps comprising a step of adsorbing a gaseous hydrogenated compound or a gaseous halogenated compound, such as arsine, phosphine, or

pound or the gaseous halogenated compound, such as arsine, phosphine, or boron trifluoride and the heating temperature to set the pressure inside the sealed space to not more than atmospheric pressure, the gaseous compound can be prevented from leaking outward at the time of expelling in the expelling step. Therefore, impurities in the activated carbon can be safely removed.

[0044] The activated carbon is treated by a series of steps comprising a step of adsorbing a gaseous hydrogenated compound or a gaseous halogenated compound upon bringing the gaseous compound into contact with the activated carbon in advance in a sealed space, a step of accelerating a reaction of a system passing through the adsorbing step, and a step of expelling the gaseous compound passing through the reaction accelerating step from the sealed space. When a gaseous hydrogenated compound or a gaseous halogenated compound of a type which is the same as or different from the above-mentioned gaseous compound is stored upon being adsorbed to the activated carbon thus treated, one or more impurity gases can be prevented from being generated by contact between the activated carbon and the gaseous compound, and the purity of the stored gaseous compound can be prevented from being decreased. Various changes and modifications of the above-mentioned method and apparatus can be made within the scope of the present invention as set forth in the accompanying claims.

[0045] For example, the amount of the activated carbon packed into the container may be suitably selected in relation to the amount of the gaseous compound, such as arsine, to be stored. The gaseous compound which is brought into contact with the activated carbon in advance in the sealed space and the gaseous compound to be stored need not be necessarily the same. For example, phosphine or boron trifluoride used as an ion implantation gas in a step of doping semiconductors may be used as the gaseous compound which is brought into contact with the activated carbon in advance in the sealed space, and arsine may be used as the gaseous compound to be stored after impurities in the activated carbon are forced to be removed.

[0046] In the method and the apparatus according to the present invention, in adsorbing the gaseous hydrogenated compound or the gaseous halogenated compound to the activated carbon and storing the adsorbed gaseous compound, and then delivering the gaseous compound, when a heating unit is provided to heat the activated carbon to which the gaseous compound is adsorbed, the adsorption capacity of the gaseous compound in the activated carbon is reduced by the heating, thereby making it possible to increase the amount of the gaseous compound which can be delivered under the same pressure. Consequently, the amount of the stored gaseous compound which can be effectively utilized is increased.

[0047] In heating the activated carbon to which the gaseous compound is adsorbed, as described above, the heating temperature is preferably not less than 30°C which is the temperature of a general operating environment where the apparatus is employed, more preferably not less than 40°C, and still more preferably 50°C to 200°C. It is not preferable that the heating temperature exceeds 200°C because the gaseous compound such as arsine self-decomposes.

[0048] In the method and the apparatus in which the heating unit is thus provided to heat the activated carbon to which the gaseous compound is adsorbed, it is also preferable to use, as the above-mentioned activated carbon, activated carbon treated by a series of steps comprising a step of adsorbing a gaseous hydrogenated compound or a gaseous halogenated compound upon bringing the gaseous compound into contact with the activated carbon in advance in a sealed space, a step of accelerating a reaction of a system passing through the adsorbing step, and a step of expelling the gaseous compound passing through the reaction accelerating step from the sealed space.

[0049] An example of a method of producing the activated carbon utilized in the present invention will be described in detail below.

[0050] Generally, a phenol resin used for producing the activated carbon is roughly classified into a resol resin, a novolak resin, other special phenol resins, and their modified products. The phenol resin may be any phenol resin, and is not particularly limited. For example, granular or powdery special phenol resins disclosed in Examined Published Japanese Patent Application Nos. 62-30210 and 62-30212 can be suitably used. The outline of the method of producing the special phenol resin is as follows.

[0051] Phenol or a mixture of phenol and a nitrogen-containing compound, such as urea, melamine or aniline, is added to a combined aqueous solution comprising 15 to 22 % by weight of hydrochloric acid and 7 to 15 % by weight of formaldehyde at a ratio of not more than 1/15 of the mixed aqueous solution while stirring the combined aqueous solution at room temperature. The stirring is stopped before white turbidity appears in a reaction system, and the system is allowed to stand. A granular phenol resin in pink is formed and is settled in the reaction system while the system is allowed to stand. The entire reaction system is then heated while being stirred again, is raised to a temperature of 40 to 90°C to complete the reaction, is then washed with water, and is subsequently neutralized with aqueous ammonia, followed by washing with water, dehydration and drying. Much of the granular phenol resin thus obtained is composed of primary particles having a particle diameter of 0.1 to 150 µm or their secondary agglomerates.

[0052] The phenol resin thus obtained is special phenol resin powder which differ in properties from a resol resin and a novolak resin, and can be suitably used as the phenol resin powder used for producing the activated carbon utilized in the present invention. When the phenol resin is heated and refluxed in 500 ml of anhydrous methanol, a methanol solubility S indicated by the following equation can be used as an index representing reactivity:

ylene ether bond, or such a reaction that dehydration occur between a methylol group and an alcohol to form an ether.

[0065] The liquid melamine resin can be classified into a water-soluble resin and an oil-soluble resin. The water-soluble resin can be generally produced using methanol as an alcohol. On the other hand, the oil-soluble resin is also called a butylated melamine resin, and is generally produced using butanol as an alcohol.

[0066] In producing the activated carbon, the liquid melamine resin used as a binder may be either water-soluble or oil-soluble, and those produced by known processes can be used.

[0067] In fabricating the activated carbon, a polyvinyl alcohol used as the binder preferably has a polymerization degree of 100 to 5000 and a saponification degree of not less than 70 %, and those partially modified by a carboxyl group or the like are also suitably used.

[0068] In producing the activated carbon, the phenol resin powder and the binder component are mixed with each other, and a mixture obtained is then granulated, to obtain a granular formed product. The amount of the binder to be mixed with the phenol resin powder is in the range of 5 to 90 parts by weight, preferably 10 to 60 parts by weight, and more preferably 20 to 40 parts by weight per 100 parts by weight of the phenol resin powder. The reason why the amount of the binder is thus in the range of 5 to 90 parts by weight per 100 parts by weight of the phenol resin powder is that if the amount of the binder is less than 5 parts by weight, the workability at the time of the granulation is lowered to make extraction by a dice difficult, resulting in some problems. For example, the granulated product is not uniform in shape and is low in strength, and powder is liable to be generated. On the other hand, when the amount of the binder is more than 90 parts by weight, the workability at the time of the granulation is lowered, and the connectivity of pores in a pellet after carbonization and activation is lowered to degrade the performance of the binder as an adsorbent.

[0069] In mixing the phenol resin powder and a binder component with each other, a commercially available mixing and stirring machine such as a ribbon mixer, a V-type mixer, a cone mixer, or a kneader is used at room temperature or under heating.

[0070] Other additives can be also added in addition to the phenol resin and the binder component. For example, it is also possible to add a suitable amount of starch, crystalline cellulose powder, methylcellulose, water, and a solvent, for example, and add a small amount of coke and coconut shell, for example.

[0071] Furthermore, in producing the activated carbon, it is possible to add a surface active agent, such as ethylene glycol, polyoxyethylene, alkylether, polyoxyethylene fatty acid ester, or ammonium polycarboxylic acid salt, a crosslinking agent such as polyvinyl alcohol, a plasticizer for extruding granulation, and so forth in a range in which the properties of the activated carbon are not degraded in order to improve the workability at the time of mixing and at the time of granulation.

[0072] The phenol resin, the binder component, and so forth are formed into a granular product after being uniformly mixed with one another, as described above. The formation into a granular product can be performed by using a uniaxial or biaxial wet extruding granulator, a vertical granulator such as a basket ryuzer (commercially available), and a semidry disk pelletter, for example. Further, the formation into the granular product is generally performed at room temperature.

However, it may be performed under heating depending on cases. The granular product thus obtained is generally dried in a temperature range of approximately 50 to 400°C, to obtain a granular formed product.

[0073] The granular formed product is generally in the shape of a columnar or spherical pellet, and is adjusted at the time of granulation such that the shape of the pellet after carbonization and activation becomes a predetermined shape.

[0074] In producing the activated carbon utilized in the present invention, the granular formed product obtained in the above-mentioned manner or a carbide obtained by heat-treating the granular formed product under a non-oxidation atmosphere in a temperature range of 500 to 900°C is used, and is subjected to activation treatment in a temperature range of 700 to 1100°C in a range in which a weight decrease rate based on the carbide is 5 to 40 %.

[0075] In heat-treating the granular formed product under the non-oxidation atmosphere in the temperature range of 500 to 900°C, as described above, to obtain the carbide, heat-treatment is carried out under a non-oxidation atmosphere such as nitrogen, argon, or helium using a heat treatment apparatus such as an electric furnace or an external heating gas furnace. The temperature at which heat-treatment is carried out is generally 500 to 900°C, as described above, preferably 550 to 850°C, and more preferably 600 to 800°C. The reason for this is that activation cannot be efficiently performed because the activation rate in the subsequent activation treatment step becomes low if the temperature at which heat-treatment is carried out is higher than 900°C, while the granular formed product is difficult to sufficiently carbonize because the temperature is low and the rate at which the granular formed product is carbonized becomes low if the temperature is lower than 500°C.

[0076] A temperature region where the granular formed product or the carbide obtained by the heat treatment is subjected to activation treatment is generally 700 to 1100°C, preferably 800 to 1000°C, and more preferably 850 to 950°C. The reason for this is that the pore volume in the obtained activated carbon is decreased by thermal shrinkage, and the surface of the activated carbon is oxidized to reduce the abrasion resistance if the temperature at which activation treatment is carried out is higher than 1000°C, while the activation is not sufficiently performed to reduce the adsorptivity in the obtained activated carbon if the temperature is lower than 700°C.

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of not more than 0.01 mmHg. Further, the test container is gradually heated to a temperature of 350°C from outside by a heating device, and is successively evacuated to a pressure of not more than 0.01 mmHg with the vacuum pump. Thereafter, the test container is returned to an ordinary temperature by being allowed to stand.

[0087] Arsine is then fed into the test container via the cut-off valve while maintaining the test container at a constant temperature of 20°C by an incubator, and is introduced into the test container, while adjusting the pressure inside the test container to 700 mmHg which is not more than atmospheric pressure, until it is absorbed no more. The weight of the test container at this time is taken as W4.

[0088] The weight of the test container after 20 days is then measured while maintaining the test container at a constant temperature of 20°C by an incubator. The weight of the test container at this time is taken as W5. The value of (W4 - W5) is calculated, to confirm that there is no difference due to leakage and read the internal pressure.

(3) Method of Measuring Amount of Adsorbed Arsine under Plural Pressures

[0089] A test container made of stainless steel having an inner diameter of 30 mm, a length of 150 mm, and an internal volume of 100 ml which has a diaphragm cut-off valve provided at its one end is previously weighed by a chemical balance. The weight of the test container at this time is taken as W6.

[0090] After an adsorbent used for a test is then packed into the test container, the test container is connected to a vacuum pump via the cut-off valve and is evacuated to a pressure of not more than 0.01 mmHg. Further, the test container is gradually heated to a temperature of 350°C from outside by a heating device, and is successively evacuated to a pressure of not more than 0.01 mmHg with the vacuum pump. Thereafter, the test container is returned to an ordinary temperature by being allowed to stand, and is weighed again. The weight of the test container at this time is taken as W7.

[0091] Arsine is then fed into the test container via the cut-off valve while maintaining the test container at a constant temperature of 25°C by an incubator, and is introduced into the test container, while adjusting the pressure inside the test container to 10, 20, 30, 50, 100, 200, 300, 400, 500, 600, and 700 mmHg which are not more than atmospheric pressure, until it is absorbed no more at the time of each of the pressures. The weight of the test container at this time is taken as Wn. The amount of the adsorbent is determined by (W7 - W6), and the amount of the adsorbed arsine is determined by (Wn - W7).

(4) Method of Measuring Tensile Strength

[0092] The tensile strength of particles of activated carbon is measured by a Kiya-type hardness tester. The tensile strength to be evaluated by measuring the strength is calculated by the following equation from a load P [kg], a particle diameter d[cm], and a particle length l [cm] in a case where the particles are pulverized:

$$\text{Tensile strength : } \sigma[\text{kg/cm}^2] = 2P/(\pi \cdot d \cdot l)$$

(5) Method of Measuring Specific Surface Area of Activated Carbon

[0093] Approximately 0.1 g of each activated carbon is accurately weighed, and is then put in a cell dedicated to a high precision full-automatic gas adsorber BELSORP28 (manufactured by Nippon Bel Co., Ltd.). Nitrogen is adsorbed using the adsorber, to find a specific surface area by the BET (Brunauer-Emmett-Teller) method.

(6) Method of Measuring Pore Volume

[0094] In measuring the pore volume of pores of an adsorbent, the pore volume of pores having a pore diameter in a range of 0.01 to 10 μm is measured by a method of mercury penetration using a porosimeter (Poresizer 9310 manufactured by Shimadzu Corporation), and the pore volume of pores having a pore diameter of not more than 10 nm is measured by measuring nitrogen adsorption using a full-automatic gas adsorption measuring device (BELSORP 28 manufactured by Nippon Bel Co., Ltd.). Specifically, the pore volume of pores having a pore diameter in a range of 2 to 10 nm is found by conducting a D-H analysis of an adsorption isotherm of nitrogen gas at 77 K, and the pore volume of pores having a pore diameter of not more than 2 nm is found by conducting an analysis using an MP method from a t-plot of an adsorption isotherm of nitrogen gas at 77 K.

(7) Method of Measuring Ash Content

[0095] 1 g of a specimen dried at 105°C for two hours is precisely weighed in a platinum crucible, is ashed at 700°C

(Table 2)

| properties of activated carbon | | | | | | | | | | | |
|--------------------------------|-----------------------------|----------------------|--------------------------|-------------------------------------------|--------------------------------------------------------|----------------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------------|----------------------------------------|------------------------|---------------------|
| sample | activation temperature (°C) | activation time (hr) | weight decrease rate (%) | specific surface area (m ² /g) | pore properties | | | | tensile strength (kg/cm ²) | packing density (g/cc) | bulk density (g/cc) |
| | | | | | volume of pores having a diameter of 0.01-10 μm (cc/g) | volume of pores having a diameter of not more than 10nm (cc/g) | volume of pores having a diameter of 0.6-0.8nm (cc/g) | ratio of volume of pores having a diameter of 0.6-0.8nm (%) | | | |
| 1 | 750 | 1.5 | 22 | 856 | 0.286 | 0.368 | 0.339 | 92 | 56 | 0.68 | 0.93 |
| 2 | 900 | 1.5 | 31 | 1074 | 0.273 | 0.480 | 0.374 | 78 | 83 | 0.59 | 0.70 |
| 3 | 950 | 1.5 | 37 | 1248 | 0.350 | 0.605 | 0.472 | 78 | 45 | 0.56 | 0.58 |
| 4 | 980 | 1.5 | 41 | 1460 | 0.390 | 0.607 | 0.473 | 78 | 40 | 0.48 | 0.44 |
| 5 | 1000 | 1.5 | 47 | 1770 | 0.477 | 0.820 | 0.459 | 56 | 27 | 0.38 | 0.31 |
| 6 | 1000 | 2.0 | 64 | 2143 | 0.571 | 1.100 | 0.055 | 5 | 6 | 0.29 | 0.28 |
| 7 | 700 | 1.5 | 18 | 675 | 0.261 | 0.287 | 0.235 | 82 | 66 | 0.74 | 0.92 |

[0102] The samples 1 to 7 obtained in the above-mentioned manner and coconut shell activated carbon for gas adsorption (general activated carbon) generally used were used, to find the amount of adsorbed arsine and the amount

test containers C1 to C4.

[0110] It will be clarified that impurities are produced by a reaction between arsine or phosphine and the sample 2.

(1) Initial Vacuum Treatment Step

[0111] An initial vacuum treatment step was first carried out such that oxygen, nitrogen, water, etc. would be removed from the test container and the sample 2 which are exposed to air.

[0112] In the initial vacuum treatment step, the inlet and outlet cut-off valves CV1 to CV4 and the cut-off valve V4 are opened, and each of the test containers C1 to C4 is evacuated to a pressure of 0.1 mmHg with the vacuum pump P1 to expel air from the test container, and the cut-off valve V4 is then closed.

[0113] The cut-off valve V1 is then opened, to inject helium which is an inert gas into each of the test containers C1 to C4 from the gas source R3 until the pressure inside the test container is approximately atmospheric pressure, and the cut-off valve V1 is then closed. Thereafter, the cut-off valve V4 is opened again, to evacuate each of the test containers C1 to C4 to a pressure of approximately 0.1 mmHg. Since helium is effective in accelerating the replacement of air in each of the test containers C1 to C4, the injection of the helium may be suitably repeated several times. It may be confirmed that oxygen, nitrogen, carbon monoxide and carbon dioxide which are impurities are not generated by opening the cut-off valve V1, injecting helium, then introducing helium gas into the analyzer A1 via the cut-off valve V6 to conduct an analysis. Although helium is adsorbed to the sample 2 by being injected, no impurities are generated by the adsorption of helium.

[0114] Each of the test containers C1 to C4 is then continuously evacuated while being heated to a predetermined temperature of 300°C to 350°C, respectively, by the electric heater units, to close the cut-off valve V4, while opening the cut-off valve V5 at the time point where the degree of vacuum is approximately 0.1 mmHg. At this time, the test container is evacuated to a high pressure of not more than 10^{-5} mmHg by the molecular turbo pump P2. Finally, the inlet and outlet cut-off valves CV1 to CV4 and the cut-off valve V5 are closed, to terminate the initial vacuum treatment step. After each of the test containers C1 to C4 is allowed to stand until it is returned to an ordinary temperature, the weight W8 of the test container is weighed.

(2) Step of Injecting Preliminary Arsine or Preliminary Phosphine

[0115] While maintaining each of the test containers C1 to C4 at 20°C, opening the inlet and outlet cut-off valves CV1 to CV4 and the cut-off valve V2 or V3, and opening the cut-off valve V7, to measure the pressure inside the test container using the pressure gauge G1, preliminary arsine or preliminary phosphine is injected into the test container until the pressure inside thereof is approximately 20 mmHg. At this time, the temperatures inside the test containers C1, C2, C3, and C4 are maintained upon being respectively heated to 50°C, 100°C, 150°C, and 200°C using the temperature control units.

[0116] In order to measure impurities generated in each of the test containers C1 to C4 and the pressure inside thereof, the test container is suitably communicated to the analyzer A1 and the pressure gauge G1.

[0117] While heating each of the test containers C1 to C4 to maintain the temperature inside thereof at 200°C, the test container is evacuated to a pressure of 10^{-5} mmHg using the vacuum pump P1 and the molecular turbo pump P2, to expel the preliminary arsine or the preliminary phosphine containing impurities from the test container. At this time, the preliminary arsine or the preliminary phosphine containing impurities can be accumulated in the buffer space provided at the upper part of each of the test containers V1 to C4, so that it is smoothly expelled. After each of the test containers C1 to C4 is allowed to stand until it is returned to an ordinary temperature, the weight W9 of the test container is weighed.

(3) Step of Adsorbing Arsine for Storage or Phosphine for Storage

[0118] While maintaining each of the test containers C1 to C4 at 20°C, opening the cut-off valves CV1 to CV4 and the cut-off valve V2 or V3, and opening the cut-off valve V7, to measure the pressure inside the test container using the pressure gauge G1, arsine for storage or phosphine for storage is injected into the test container until the pressure inside thereof is approximately 400 mmHg, and is adsorbed to the sample 2 in the test container. After it is confirmed by the analyzer A1 that no impurities are generated in each of the test containers C1 to C4, the inlet and outlet cut-off valves CV1 to CV4 are closed, to measure the weight W10 of the test container, and calculate the weight of the gas (W10 - W9) stored in the test container.

(4) Results of Experiments

[0119] Figs. 3 to 5 show the results of experiments in a case where arsine is used, and Fig. 6 shows the results of

carbon under pressures at a temperature of 25°C. The results were shown in Table 4.

(Table 4)

| Amount of adsorbed arsine per liter of activated carbon at 25°C | | |
|-----------------------------------------------------------------|-------------------------------|--------------------------------|
| arsine pressure (Torr) | amount of adsorbed arsine (g) | |
| | sample 2 | coconut shell activated arsine |
| 10 | 93 | 64 |
| 20 | 116 | 77 |
| 30 | 131 | 88 |
| 40 | 143 | 97 |
| 50 | 153 | 104 |
| 100 | 189 | 126 |
| 200 | 234 | 158 |
| 300 | 265 | 178 |
| 400 | 290 | 198 |
| 500 | 310 | 210 |
| 600 | 328 | 225 |
| 700 | 344 | 234 |

[0129] As a result, in the activated carbon that is the sample 2 satisfying the above-mentioned conditions, the amount of adsorbed arsine was much higher, as compared with that in the general coconut shell activated carbon for gas adsorption.

(Example 4)

[0130] The apparatus for gas storage shown in Fig. 1 was employed, to measure the weight W1 of a test container in a case where an adsorbent was packed into the test container in conformity with a method of measuring the amount of adsorbed arsine and the amount of released arsine in the item (1) in the above-mentioned embodiment, and then measure the weight W2 of the test container in a case where an arsine gas was injected therein under conditions of 700 mmHg while maintaining the temperature inside the test container at 20°C. The result of calculation of the amount of adsorbed arsine (= W2 - W1) was 260 g.

[0131] The test container in which the arsine gas was injected was evacuated to a pressure of 20 mmHg with a vacuum pump, as described above, to release the arsine gas outward from the test container. The weight W3 of the test container at this time was measured, to find the amount of released arsine (= W2 - W3) and the amount of remaining arsine (= W3 - W1). Further, the releasing ratio was found by the following equation from the amount of adsorbed arsine and the amount of released arsine.

[0132] Releasing ratio (%) = (amount of released arsine / amount of adsorbed arsine) X 100

[0133] In a case where the temperature of the test container in which the arsine gas was injected was set to 20°C, 35°C, 50°C, 100°C, and 150°C, to release the arsine gas from the test container, the amount of remaining arsine, the amount of released arsine, and the releasing ratio were found. The results were shown in Table 5.

(Table 5)

| heated temperature (°C) | amount of remaining arsine (g) | amount of released (g) | releasing ratio (%) |
|-------------------------|--------------------------------|------------------------|---------------------|
| 20 (not heated) | 105 | 155 | 59.6 |
| 35 | 90 | 170 | 65.4 |
| 50 | 79 | 181 | 69.6 |
| 100 | 57 | 203 | 78.1 |
| 150 | 46 | 214 | 82.3 |

Claims

1. A method of storing and delivering a gaseous hydrogenated compound or a gaseous halogenated compound, which is **characterized in that** a gaseous hydrogenated compound or a gaseous halogenated compound in a predetermined amount is stored upon being adsorbed to high-purity activated carbon under a storage environment at a pressure which is not more than atmospheric pressure by being brought into contact with the activated carbon, and is evacuated to a negative pressure in order to desorb at least a part of said adsorbed gaseous compound and deliver the part to a work environment.
2. The method according to claim 1, wherein the storage environment is heated when at least a part of a particular gaseous hydrogenated compound or gaseous halogenated compound, which is adsorbed to said activated carbon, is desorbed and is delivered.
3. The method according to claim 1 or 2, wherein said activated carbon is composed of a phenol resin as a main raw material.
4. The method according to any one of claims 1 to 3, wherein said activated carbon is a granular carbon formed product obtained by bonding activated particles formed by carbonizing phenol resin powder, which has a specific surface area of 700 to 1500 m²/g, has pores having a pore diameter of 0.01 to 10 μm, the pore volume of which is 0.1 to 1.0 cc/g, has pores having a pore diameter of not more than 10 nm, the pore volume of which is 0.20 to 0.80 cc/g, and containing not less than 75 % by volume pores having a power diameter of 0.6 to 0.8 nm, has a bulk density of 0.4 to 1.1 g/cc, has a packing density of 0.30 to 0.70 g/cc, has an ash content of not more than 1.0 %, and has a tensile strength of not less than 30 kg/cm².
5. A method of treating activated carbon by a series of steps comprising a step of adsorbing a gaseous hydrogenated compound or a gaseous halogenated compound upon bringing the gaseous compound into contact with activated carbon in advance in a sealed space, a step of accelerating a reaction of a system passing through the adsorbing step, and a step of expelling the gaseous compound passing through the reaction accelerating step from said sealed space, to prevent, when a gaseous hydrogenated compound or a gaseous halogenated compound of a type which is the same as or different from that of said gaseous compound is adsorbed to be stored, the purity of the stored gaseous compound from being decreased due to one or more impurity gases generated by contact between the activated carbon and the stored gaseous compound.
6. The method according to claim 5, wherein in the reaction accelerating step, the amount and/or the heating temperature of the gaseous hydrogenated compound or the gaseous halogenated compound which is packed into the sealed space are selected.
7. The method according to claim 5 or 6, wherein the amount and/or the heating temperature of the gaseous hydrogenated compound or the gaseous halogenated compound which is packed into the sealed space are selected such that the pressure inside the sealed space in the expelling step is not more than atmospheric pressure.
8. The method according to any one of claims 5 to 7, wherein a buffer space for smoothly expelling in said expelling step the impurity gases included in the gaseous hydrogenated compound or the gaseous halogenated compound by said reaction accelerating step is provided in the sealed space.
9. A method of storing and delivering a gaseous hydrogenated compound or a gaseous halogenated compound, which is **characterized in that** a gaseous hydrogenated compound or a gaseous halogenated compound in a predetermined amount is stored upon being adsorbed to activated carbon treated using the method according to any one of claims 5 to 8 by being brought into contact with the activated carbon under a storage environment at a pressure which is not more than atmospheric pressure, and is evacuated to a negative pressure in order to desorb at least a part of the adsorbed gaseous compound and deliver the part to a work environment.
10. The method according to claim 9, wherein the storage environment is heated when at least a part of the gaseous hydrogenated compound or the gaseous halogenated compound, which is adsorbed to said activated carbon, is desorbed and is delivered.
11. The method according to claim 9 or 10, wherein said activated carbon is composed of a phenol resin as a main raw material.

compound, which is **characterized in that** activated carbon which is a granular carbon formed product obtained by bonding activated particles formed by carbonizing phenol resin powder, which has a specific surface area of 700 to 1500 m²/g, has pores having a pore diameter of 0.01 to 10 μm, the pore volume of which is 0.1 to 1.0 cc/g, has pores having a pore diameter of not more than 10 nm, the pore volume of which is 0.20 to 0.80 cc/g, and containing not less than 75 % by volume pores having a power diameter of 0.6 to 0.8 nm, has a bulk density of 0.4 to 1.1 g/cc, has a packing density of 0.30 to 0.70 g/cc, has an ash content of not more than 1.0 %, and has a tensile strength of not less than 30 kg/cm² is used, a gaseous hydrogenated compound or a gaseous halogenated compound in a predetermined amount is stored upon being adsorbed to said activated carbon under a storage environment at a pressure which is not more than atmospheric pressure by being brought into contact with the activated carbon, and is evacuated to a negative pressure in order to desorb at least a part of said adsorbed gaseous compound and deliver the part to a work environment.

2. The method according to claim 1, wherein the storage environment is heated when at least a part of a particular gaseous hydrogenated compound or gaseous halogenated compound, which is adsorbed to said activated carbon, is desorbed and is delivered.
3. (Cancelled)
4. (Cancelled)
5. A method of treating activated carbon by a series of steps comprising a step of adsorbing a gaseous hydrogenated compound or a gaseous halogenated compound upon bringing the gaseous compound into contact with activated carbon in advance in a sealed space, a step of accelerating a reaction of a system passing through the adsorbing step, and a step of expelling the gaseous compound passing through the reaction accelerating step from said sealed space, to prevent, when a gaseous hydrogenated compound or a gaseous halogenated compound of a type which is the same as or different from that of said gaseous compound is adsorbed to be stored, the purity of the stored gaseous compound from being decreased due to one or more impurity gases generated by contact between the activated carbon and the stored gaseous compound.
6. The method according to claim 5, wherein in the reaction accelerating step, the amount and/or the heating temperature of the gaseous hydrogenated compound or the gaseous halogenated compound which is packed into the sealed space are selected.
7. The method according to claim 5 or 6, wherein the amount and/or the heating temperature of the gaseous hydrogenated compound or the gaseous halogenated compound which is packed into the sealed space are selected such that the pressure inside the sealed space in the expelling step is not more than atmospheric pressure.
8. The method according to any one of claims 5 to 7, wherein a buffer space for smoothly expelling in said expelling step the impurity gases included in the gaseous hydrogenated compound or the gaseous halogenated compound by said reaction accelerating step is provided in the sealed space.
9. A method of storing and delivering a gaseous hydrogenated compound or a gaseous halogenated compound, which is **characterized in that** a gaseous hydrogenated compound or a gaseous halogenated compound in a predetermined amount is stored upon being adsorbed to activated carbon treated using the method according to any one of claims 5 to 8 by being brought into contact with the activated carbon under a storage environment at a pressure which is not more than atmospheric pressure, and is evacuated to a negative pressure in order to desorb at least a part of the adsorbed gaseous compound and deliver the part to a work environment.
10. The method according to claim 9, wherein the storage environment is heated when at least a part of the gaseous hydrogenated compound or the gaseous halogenated compound, which is adsorbed to said activated carbon, is desorbed and is delivered.
11. The method according to claim 9 or 10, wherein said activated carbon is composed of a phenol resin as a main raw material.
12. The method according to any one of claims 9 to 11, wherein said activated carbon is a granular carbon formed product obtained by bonding activated particles formed by carbonizing phenol resin powder, which has a specific surface area of 700 to 1500 m²/g, has pores having a pore diameter of 0.01 to 10 μm, the pore volume of which

Fig 1

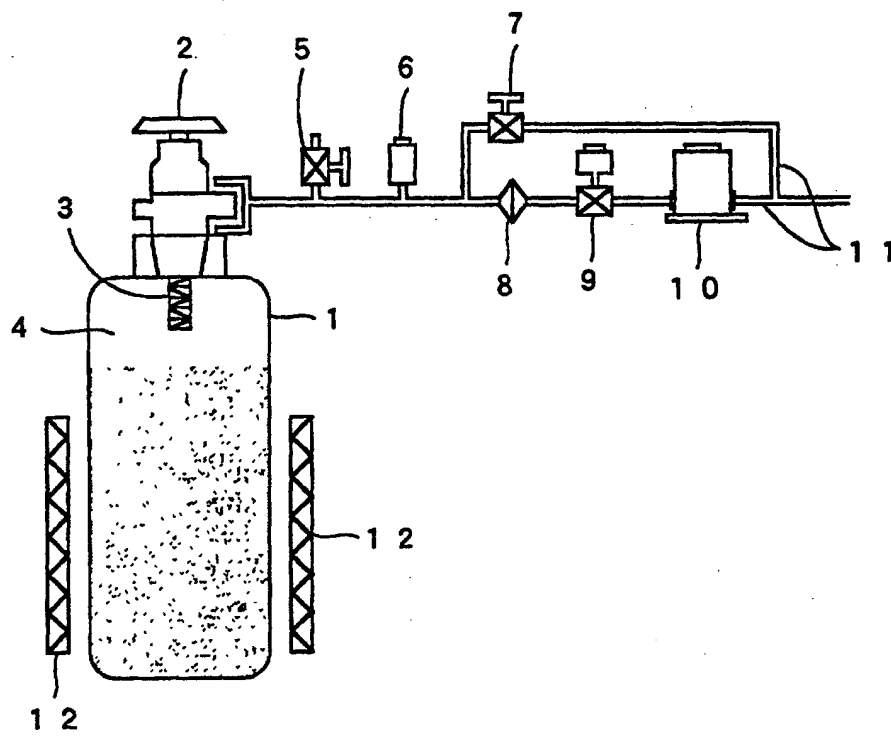


Fig 3

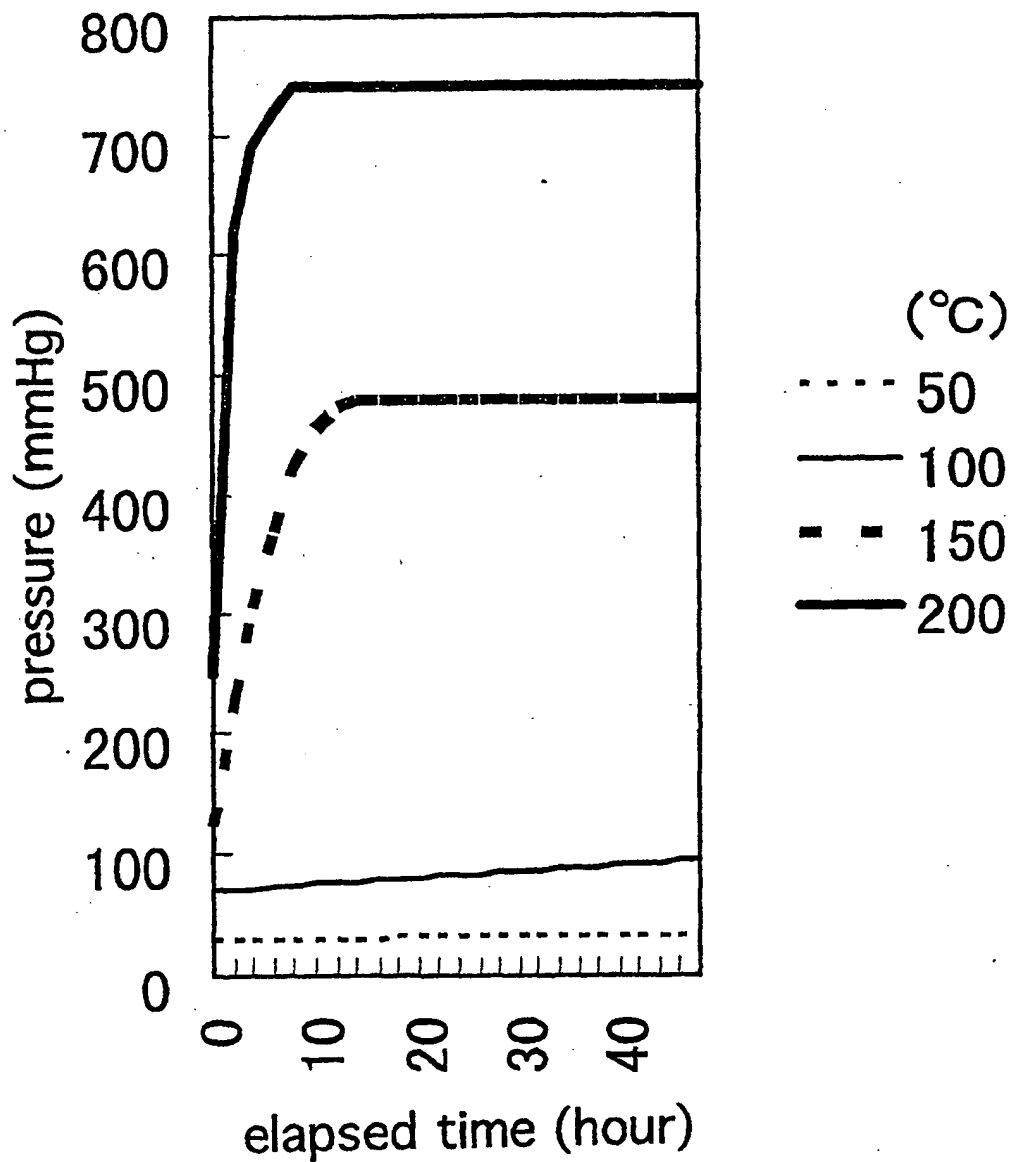
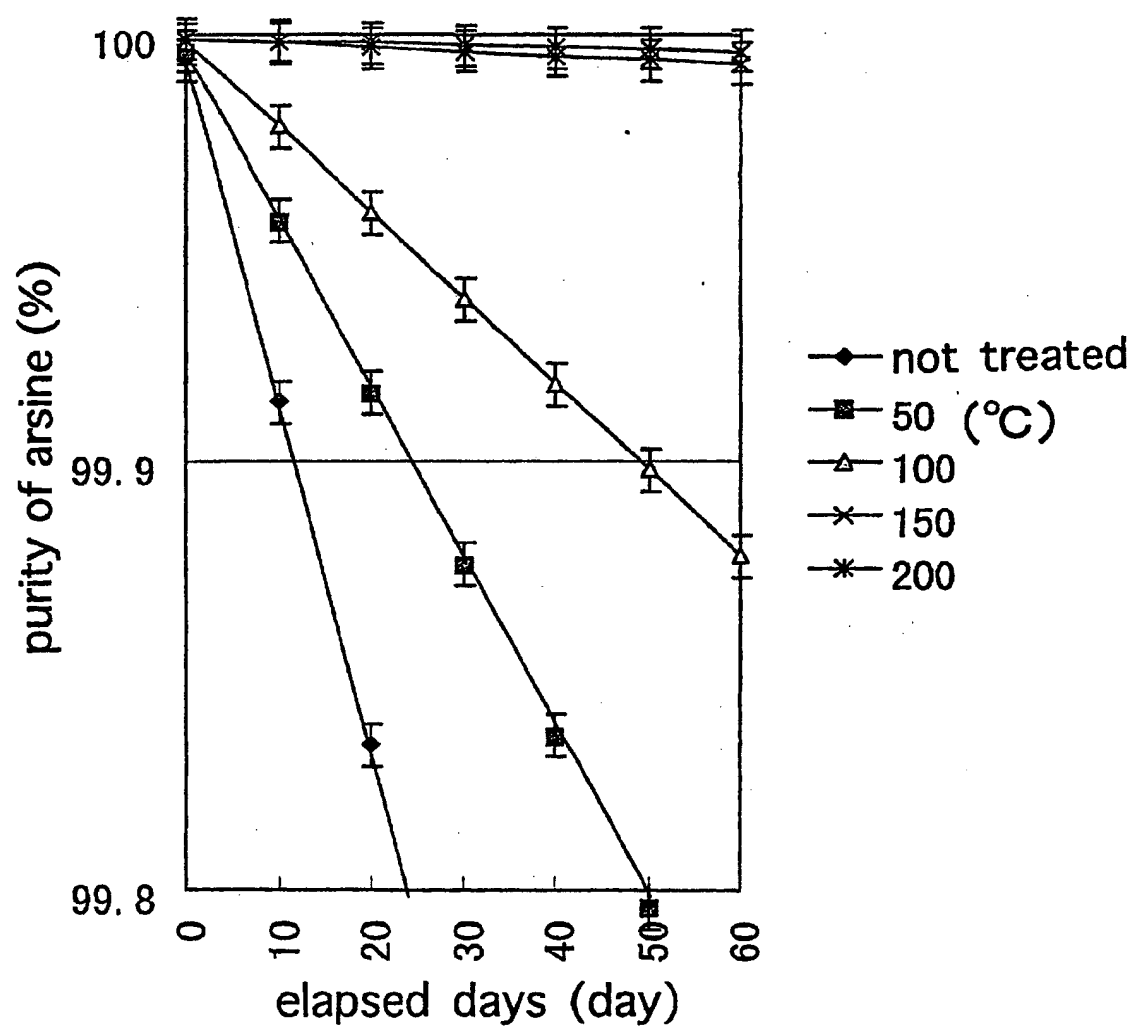


Fig 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/03644

| A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ B01J20/20, C01B31/08, F17C11/00 According to International Patent Classification (IPC) or to both national classification and IPC | | |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁶ B01J20/00-20/34, C01B31/08, F17C11/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Torokai Jitsuyo Shinan Koho 1994-1998 Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Keisai Koho 1996-1998 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y | WO, 96/11739, A1 (ATMI ECOSYS CORPORATION), 25 April, 1996 (25. 04. 96), Claims ; page 13, line 15 to page 17, line 6 & US, 5707424, A & US, 5704965, A & US, 5704967, A & AU, 9734572, A & EP, 854749, A & US, 5518528, A & AU, 9538300, A & EP, 785817, A & JP, 10-503268, A & KR, 97702745, A | 1-4, 14-17 |
| Y | JP, 8-224468, A (Kanebo, Ltd.), 3 September, 1996 (03. 09. 96), Claims ; page 2, right column, line 45 to page 3, left column, line 8 ; page 4, left column, line 31 to right column, lines 17, 28 to page 5, left column, line 1 ; Table 1 (Family: none) | 1-4, 14-17 |
| A | JP, 9-210295, A (Tokyo Gas Co., Ltd.), 12 August, 1997 (12. 08. 97), Claims & CA, 2196381, A & US, 5787605, A | 1-21 |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex. | | |
| * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family | | |
| Date of the actual completion of the international search 6 November, 1998 (06. 11. 98) | | Date of mailing of the international search report 17 November, 1998 (17. 11. 98) |
| Name and mailing address of the ISA/ Japanese Patent Office | | Authorized officer |
| Facsimile No. | | Telephone No. |

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